

Evaluating the accuracy of the Distributed Activation Energy Model for biomass devolatilization curves obtained at high heating rates



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ABSTRACT

The characteristic parameters of devolatilization, the activation energy and the frequency factor, can be obtained following different experimental approaches. In the Distributed Activation Energy Model (DAEM), these parameters are derived from several TGA curves that are typically obtained for constant, low heating rate experiments. Then, the results are used to model high heating rate processes typical of industrial combustors. In this work, a wide range of heating rates were employed to obtain different TGA curves of the biomass pyrolysis, in order to analyse the validity of DAEM when extrapolating the kinetic parameters obtained for low heating rate curves used in the laboratory to higher heating rates present in industrial applications. The TGA curves of the biomass pyrolysis employed in DAEM were varied from low heating rates (around 10 K/min, values typically found in the literature on DAEM), to high heating rates (up to 200 K/min). The differences in the activation energy and the frequency factor obtained for different heating rates, were evaluated and the validity of the model was discussed. The results show differences between the activation energy and the frequency factor obtained using low and high heating rates during the TGA tests. Therefore, if an accurate approximation is required when extrapolating the data to high heating rates, the tests should be carried out at high heating rates.

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1. Introduction

Biomass pyrolysis takes place during most of the processes related to biomass thermochemical conversion, such as production of liquid biofuels [1], synthesis gas [2], chemicals [3], or charcoal [4], becoming a key factor in most applications. The characteristic parameters that control the kinetics of biomass devolatilization are the activation energy (E_a) and the frequency factor (k_0). Several models are available in literature to describe biomass pyrolysis [5–7], and between them the Distributed Activation Energy Model (DAEM) proposed by Vand [8] has been widely used due to its simplicity and accuracy. Miura and Maki [9] simplified the model to estimate the activation energy and the corresponding frequency factor from three TGA curves obtained for different heating rates. This simplification has been used to describe the kinetics of pyrolysis for different types of biomass [10–14], coal [15,16], sewage sludge [17,18], and waste [19–21].

The heating rates employed using DAEM are usually low, in the range of 3–30 K/min, due to the higher accuracy of TGA at reduced

heating rates. Miura and Maki [9] proposed the use of heating rates of 5, 10 and 20 K/min, but Sonobe and Worasuwannarak [10] employed even lower heating rates 2, 4 and 10 K/min. Shen et al. [11] employed heating rates between 5 and 40 K/min and Soria-Verdugo et al. [18] used heating rates of 10, 15, 20 K/min. Despite of the variety of heating rates found in the literature most of the authors used heating rates below 50 K/min. As an exception, Li et al. [15] used heating rates of 20, 35, 50, 75 and 100 K/min during the devolatilization of coals and biomass in a thermogravimetric analyzer, nevertheless there is no available data for heating rates beyond 100 K/min.

In this work, a wider range of heating rates (3, 5, 10, 15, 20, 30, 50, 80, 100, 150 and 200 K/min) were employed to obtain different TGA curves, in order to analyse the validity of the simplified Distributed Activation Energy Model, when extrapolating the kinetic parameters obtained for low heating rate curves to higher heating rates. The simplified DAEM process described by Miura and Maki [9] to obtain the pyrolysis parameters was analysed for the different heating rates, hence the three TGA curves employed were varied from very low heating rates (3, 5 and 10 K/min) to higher heating rates (100, 150 and 200 K/min). The differences in the activation energy and the frequency factor were evaluated and the validity of the model was discussed.

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Nomenclature

a	heating rate (K/s)	R^2	determination coefficient of the linear fitting (-)
E_a	activation energy for a determined devolatilization rate (J/mol)	T	temperature (K)
k_0	frequency factor for a determined devolatilization rate (s^{-1})	V	volatile mass loss (%)
R	universal constant (J/mol K)	V^*	volatile content (%)
		V/V^*	devolatilization rate (%)
		ε	relative error (%)

2. Experimental procedure

The biomass employed during the tests was obtained from commercial pine pellets. The biomass characterization results of a proximate and ultimate analysis are presented in Table 1. The proximate analysis was performed in a TGA Q500 TA Instruments, while the ultimate analysis was carried out in a LECO TruSpec CHN and TruSpec S elemental analyzer. The moisture of the sample was obtained after an isothermal process at 105 °C under an inert atmosphere in the TGA, whereas the volatile content was determined heating the sample up to 900 °C under an inert atmosphere, and maintaining the temperature until no difference in the mass of the sample was observed. The ash content was measured as the constant mass of the sample remaining after an isothermal process at 550 °C under and oxidant atmosphere. Finally, the fixed carbon of the sample was obtained by difference.

The devolatilization tests were carried out in the same thermogravimetric analyzer TGA Q500 TA Instruments employed to obtain the biomass proximate analysis. During the experiments, the TGA furnace was flushed with 60 ml/min of nitrogen to maintain an inert atmosphere. The mass of the samples were 10 ± 0.5 mg and they were sieved under 100 μ m to avoid heat transfer effects, according to Di Blasi et al. [22]. A blank experiment was also run for any case studied to avoid buoyancy effects [11,12]. Each test was replicated five times to guarantee repeatability, obtaining differences always lower than 3%.

Once the sample was introduced in the TGA, it was heated up to 105 °C from room temperature, and an isothermal process was maintained during 20 min to eliminate all the moisture content. Then, the devolatilization process begins, and the temperature increases at a constant heating rate a until 600 °C. Fig. 1 shows the weight loss and the temperature versus time for the TGA analysis using heating rates a of 20 and 200 K/min during the devolatilization process. The drying process is the same for both tests so the weight loss curves collapsed during the first part of the analysis, nevertheless the different heating rates employed in the devolatilization process produced significant differences on the sample weight loss curves when the pyrolysis occurred. Depending

on the heating rate used during the devolatilization process, the time needed for the test can be very different: from 68 min for the heating rate of 20 K/min to just 45 min when using 200 K/min. Nonetheless, the weight percentage loss at the end of the devolatilization is independent of the heating rate employed. During the experiments several heating rates were employed during the devolatilization process, in a wide range: 3, 5, 10, 15, 20, 30, 50, 80, 100, 150, and 200 K/min. In the case of a heating rate of 3 K/min, 210 min were needed to perform the test.

Finally, since this work is not focused in the drying process but in the devolatilization process, the range of devolatilization can be obtained from the TGA curve (Fig. 1), defining a devolatilization rate of 0% at the end of the isothermal process at 105 °C, and 100% when the temperature is 550 °C, ensuring a constant heating rate, a , for the whole devolatilization process. Fig. 2 shows the devolatilization rate as a function of temperature for the same heating rates depicted in Fig. 1. It can be observed that most of the devolatilization process occurs between 300 °C and 400 °C, obtaining a sharp devolatilization rate typical of cellulose.

3. Simplified DAEM model

The Distributed Activation Energy Model has been proved to be an accurate method to describe the pyrolysis kinetics of biomass, obtaining a good agreement with the experimental data [10,23–25], when operating at low heating rates. The model assumes the existence of an infinite number of irreversible first order reactions occurring sequentially, with different associated activation energies, E_a . The devolatilization process can be described in the integral form by Eq. (1):

$$1 - \frac{V}{V^*} = \int_0^\infty \exp\left(-k_0 \int_0^t e^{-E/RT} dt\right) f(E) dE \quad (1)$$

where V/V^* is the devolatilization rate, R the universal constant, T the temperature for each devolatilization and $f(E)$ the distribution function of the activation energy. This equation was simplified to Eq. (2) by Miura et al. [26]

Table 1
Thermochemical characterization of the biomass employed.

Proximate analysis ^a	
Moisture (%)	3.3
Volatiles (%)	76.3
Fixed carbon ^b (%)	17
Ash (%)	3.4
Ultimate analysis ^a	
C (%)	46.13
H (%)	6.51
N (%)	0.82
S (%)	0.07
O ^b (%)	46.47

^a Wet basis.

^b Obtained by difference.

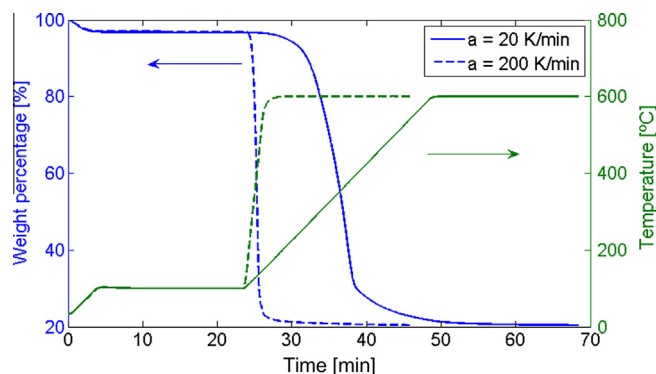


Fig. 1. Example of a thermogravimetric analysis ($a = 20$ K/min and 200 K/min).

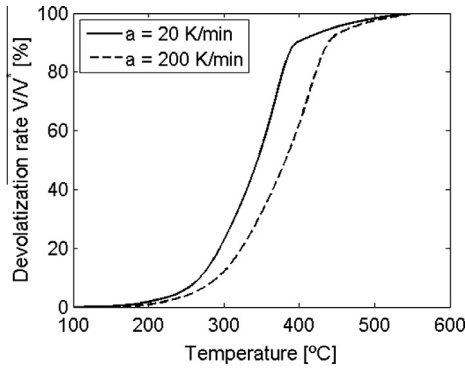


Fig. 2. Devolatilization rate against temperature ($a = 20$ K/min, 200 K/min).

$$V/V^* \cong 1 - \int_{E_a}^{\infty} f(E_a) dE_a = \int_0^{E_a} f(E_a) dE_a \quad (2)$$

The Arrhenius equation of the simplified DAEM model is:

$$\ln\left(\frac{a}{T^2}\right) = \ln\left(\frac{k_0 R}{E_a}\right) + 0.6075 - \frac{E_a}{R T} \quad (3)$$

The values of the activation energy, E_a , and the corresponding frequency factor, k_0 , present in Eq. (3) can be obtained from three different thermogravimetric curves obtained with different heating rates. Miura and Maki [9] proposed a procedure following the next steps:

- Measure and plot the devolatilization rate, V/V^* , as a function of the temperature, T , for three different heating rates, a .
- Plot $\ln(a/T^2)$ versus $1/T$ for the three different heating rates at each devolatilization rate (Arrhenius plot).
- For each V/V^* in the Arrhenius plot, linearize the data of the different heating rates and obtain E_a and k_0 from the slope and the intercept respectively.

4. Results and discussion

Thermogravimetric tests were carried out for heating rates of 3, 5, 10, 15, 20, 30, 50, 80, 100, 150, and 200 K/min, obtaining the devolatilization rates plotted in Fig. 3 for each heating rate. The devolatilization takes place at higher temperatures when increasing the heating rate, a result previously reported in the literature that can be attributed to non-isothermal pyrolysis processes [27,28].

Following the procedure proposed by Miura and Maki [9], the temperature at which each devolatilization rate occurs can be obtained from Fig. 3, for each heating rate. With these temperatures, an Arrhenius plot can be built, plotting $\ln(a/T^2)$ versus $1/T$,

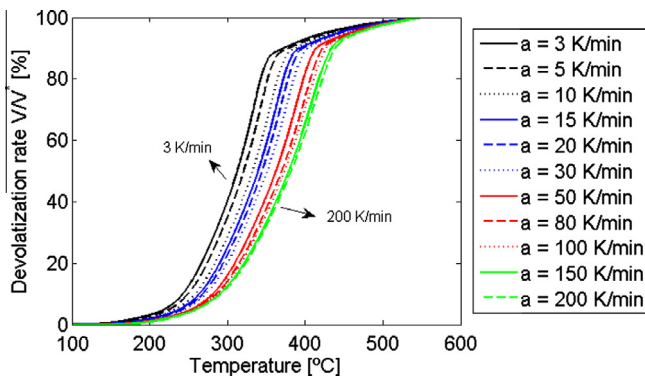


Fig. 3. Devolatilization rate versus temperature for each heating rate.

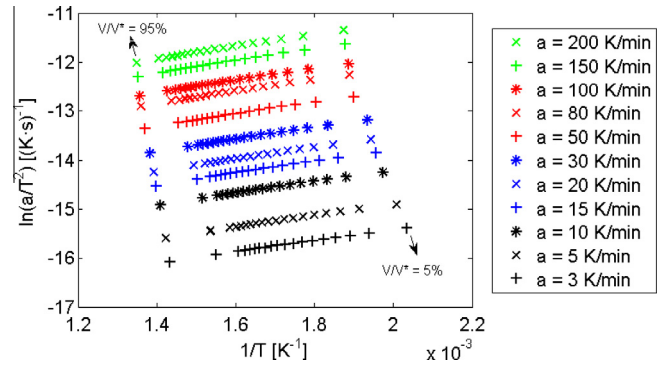


Fig. 4. Arrhenius plot for each devolatilization rate.

as shown in Fig. 4 for each devolatilization rate, with variations of 5%.

The next step in the procedure described by Miura and Maki [9] is the linearization of the results shown in the Arrhenius plot for each devolatilization rate. Analysing Fig. 4 for low devolatilization rates ($V/V^* = 5\%$), it can be observed that there is a change in the slope of the linearization curve for heating rates over 50 K/min. For high devolatilization rates this is not so evident. In order to quantify the goodness of a linear fitting of the results considering all the heating rates, the determination coefficient, R^2 , of the linear fitting is shown in Fig. 5, as a function of the devolatilization rate. The determination coefficient is found to be lower at low devolatilization rates informing of a poor linearity of the data in this zone, confirming the idea that there is a change in slope between high and low heating rates for low devolatilization rates obtained from the visual inspection of Fig. 4.

The linearization of the results shown in the Arrhenius plot (Fig. 4) was carried out regrouping the data for three different heating rates as suggested by Miura and Maki [9]. The experimental data allows to linearize the results for very low heating rates ($a = 3, 5, 10$ K/min), low heating rates ($a = 15, 20, 30$ K/min), medium heating rates ($a = 50, 80, 100$ K/min) and high heating rates ($a = 100, 150, 200$ K/min), in order to quantify the variation of slope stated above. The linearization of the results for each group of heating rates provides an slope, m , and an intercept, n , from which the activation energy, E_a , and the frequency factor, k_0 , can be easily obtained in view of Eq. (3), obtaining Eqs. (4) and (5).

$$E_a = -m \cdot R \quad (4)$$

$$k_0 = -m \cdot e^{n-0.6075} \quad (5)$$

The values of the activation energy and the frequency factor are presented in Fig. 6(a) and (b) respectively, as a function of the devolatilization rate for very low, low, medium and high heating rates.

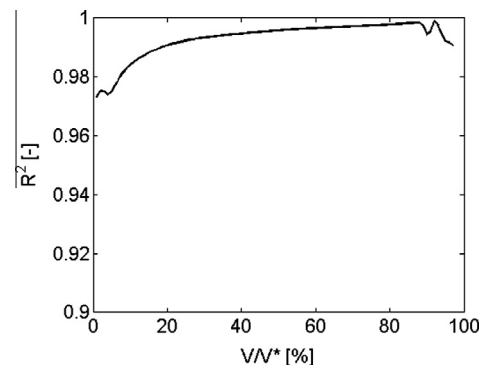


Fig. 5. Determination coefficient of the linear fitting for all the heating rates as a function of the devolatilization rate.

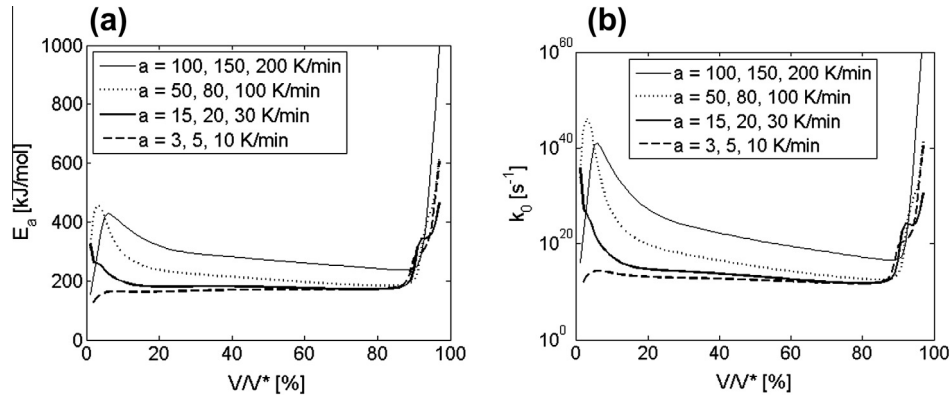


Fig. 6. (a) Activation energy and (b) frequency factor for each devolatilization rate.

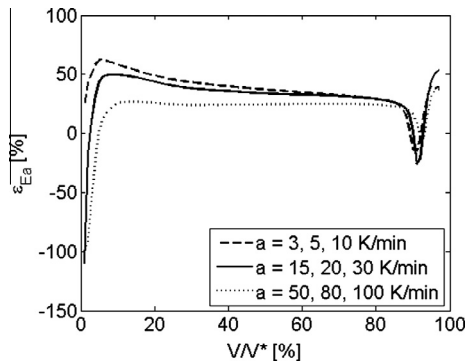


Fig. 7. Relative error of the activation energy obtained from low and high heating rates.

There is a clear difference in both the activation energy and the frequency factor when linearizing the results obtained for low and high heating rates. These parameters increase when higher heating rates are employed, confirming the existence of a higher slope in the linearization of the high heating rate TGA curves ($a = 100, 150, 200$ K/min). The difference is larger at low devolatilization rates, as established in Fig. 5.

The difference in activation energy obtained between each group of heating rates and the higher one can be analyzed by means of a relative error, ε , defined in Eq. (6).

$$\varepsilon = 100 \cdot \frac{E_{a_{ij,k}} - E_{a_{100,150,200}}}{E_{a_{100,150,200}}} \quad (6)$$

The results of the relative error in activation energy can be observed in Fig. 7. A relative error around 20% for the medium heating rates ($a = 50, 80, 100$ K/min) and around 40% for low

($a = 15, 20, 30$ K/min) and very low heating rates ($a = 3, 5, 10$ K/min) is found for devolatilization rates between 20% and 80%, that is, for most of the devolatilization process. Therefore, an error around 40% is made when determining the activation energy with low heating rate TGA curves typically found in the literature and extrapolating the results to high heating rates.

Finally, with the activation energy and the pre-exponential factor, the devolatilization curve for a heating rate of 200 K/min can be recuperated and the differences between the experimental curve obtained from the TGA and the curve recuperated using DAEM can be evaluated. The recuperation could be carried out by solving the temperature in Eq. (3) or linearizing the Arrhenius plot for each heating rate, as described in [19], with negligible differences. The differences between the TGA curve obtained for a heating rate of 200 K/min and the curve recuperated using the Distributed Activation Energy Model with low ($a = 15, 20, 30$ K/min) and high heating rates ($a = 100, 150, 200$ K/min) were analyzed by means of the devolatilization rate error and the temperature error described in Eqs. (7) and (8) respectively.

$$\varepsilon_{V/V^*} = 100 \cdot \frac{V/V_{DAEM}^* - V/V_{TGA}^*}{V/V_{TGA}^*} \quad (7)$$

$$\varepsilon_T = 100 \cdot \frac{T_{DAEM} - T_{TGA}}{T_{TGA}} \quad (8)$$

The error obtained for the devolatilization rate is plotted in Fig. 8(a). It can be observed that the DAEM recuperated curve coincided with the experimental curve when using the high heating rates ($a = 100, 150, 200$ K/min), obtaining an error close to zero. Nevertheless, when recuperating the curve with the activation energy and pre-exponential factor obtained for low heating rates

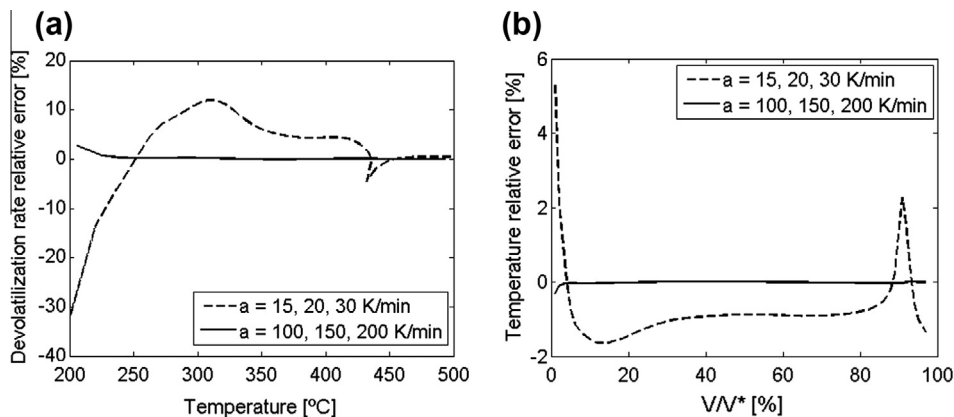


Fig. 8. Error between the TGA curve for a heating rate of 200 K/min and the curve recuperated using DAEM, (a) devolatilization rate error and (b) temperature error.

($a = 15, 20, 30$ K/min) the error in devolatilization rate is not negligible. In this case a higher error is obtained for low temperatures where the devolatilization rate is low, but for temperatures between 300 °C and 400 °C, where most of the devolatilization process occurs, the devolatilization error is between 5% and 10%. In the case of the temperature error, shown in Fig. 8(b), the value of the error is around 1% for devolatilization rates between 20% and 80%. The higher error obtained for the devolatilization rate, in comparison to that of the temperature, is motivated by the high slope shown in the devolatilization rate curve (Fig. 2) for this type of biomass.

This result shows a certain weakness of the standard process of obtaining the devolatilization parameters, E_a and k_0 , at low heating rates, as defined by Miura and Maki [9]. Even though the error obtained when extrapolating the activation energy obtained for low heating rates to higher rates can be as high as 50%, the final error obtained in the devolatilization curve is around 10% for V/V' and just 1% for T . This error should be considered for an accurate description of the devolatilization process.

5. Conclusions

The Distributed Activation Energy Model (DAEM) was applied to study pine pellets devolatilization. The model is based on TGA curves obtained for several heating rates, from low heating rates usually found in literature (3, 5, 10, 15, 20, 30, 50 K/min) to higher heating rates rarely reported (80, 100, 150, 200 K/min).

The Miura and Maki procedure was employed to obtain the activation energy and the frequency factor for each devolatilization rate. The procedure was repeated for very low heating rate curves (3, 5, 10 K/min), low heating rate curves (15, 20, 30 K/min), medium values (50, 80, 100 K/min) and high heating rates (100, 150, 200 K/min) to analyze the possible differences obtained. Such differences were quantified obtaining a relative error for the activation energy around 40% when extrapolating the results of low heating rates to higher ones. Nonetheless, when comparing the experimental devolatilization curve for a heating rate of 200 K/min with the curve obtained applying DAEM to low heating rates, the error in the devolatilization rate is under 10% and the error in temperature is just 1%.

Therefore, care should be taken when employing DAEM from low heating rate TGA curves and extrapolating the results to high heating rates typical of industrial combustors.

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References

- [1] Pütün AE, Burcu Uzun B, Apaydin E, Pütün E. Bio-oil from olive oil industry wastes: pyrolysis of olive residue under different conditions. *Fuel Process Technol* 2005;87:25–32.

- [2] Kaewluan S, Pipatmanomai S. Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidised bed gasifier. *Energy Convers Manage* 2011;52:75–84.
- [3] Orecchini F, Bocci E. Biomass to hydrogen for the realization of closed cycles of energy resources. *Energy* 2007;32:1006–11.
- [4] Prins MJ, Ptasiński KJ, Janssen FJG. Torrefaction of wood: Part 1. Weight loss kinetics. *J Anal Appl Pyrolysis* 2006;77:28–34.
- [5] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature* 1964;201:68–9.
- [6] Ubhayacar SK, Stickler DB, Von Rosenberg CW, Gannon RE. Rapid devolatilization of pulverized coal in hot combustion gases. In: 16th Symp. Combust; 1976.
- [7] Li Z, Zhao W, Meng B, Liu C, Zhu Q, Zhao G. Kinetic study of corn straw pyrolysis: comparison of two different three-pseudocomponent models. *Bioresour Technol* 2008;99:7616–22.
- [8] Vand V. A theory of the irreversible electrical resistance changes of metallic films evaporated in vacuum. *Proc Phys Soc* 1942;55:222–46.
- [9] Miura K, Maki T. A simple method for estimating $f(E)$ and $K_0(E)$ in the distributed activation energy model. *Energy Fuels* 1998;12:864–9.
- [10] Sonobe T, Worasuwannarak N. Kinetic analyses of biomass pyrolysis using the distributed activation energy model. *Fuel* 2008;87:414–21.
- [11] Shen DK, Gu S, Jin B, Fang MX. Thermal degradation mechanisms of wood under inert and oxidative environments using DAEM methods. *Bioresour Technol* 2011;102:2047–52.
- [12] Hu S, Jess A, Xu M. Kinetic study of Chinese biomass slow pyrolysis: comparison of different kinetic models. *Fuel* 2007;86:2778–88.
- [13] Cai J, Liu R. New distributed activation energy model: Numerical solution and application to pyrolysis kinetics of some types of biomass. *Bioresour Technol* 2008;99:2795–9.
- [14] Kirtania K, Bhattacharya S. Application of the distributed activation energy model to the kinetic study of pyrolysis of the fresh water algae *Chlorococcum humicola*. *Bioresour Technol* 2012;107:476–81.
- [15] Li Z, Liu C, Chen Z, Qian J, Zhao W, Zhu Q. Analysis of coals and biomass pyrolysis using the distributed activation energy model. *Bioresour Technol* 2009;100:948–52.
- [16] Günes M, Günes SK. Distributed activation energy model parameters of some Turkish coals. *Energy Sources Part A-Recov Utiliz Environ Effects* 2008;30:1460–72.
- [17] Scott SA, Dennis JS, Davidson JF, Hayhurst AN. Thermogravimetric measurements of the kinetics of pyrolysis of dried sewage sludge. *Fuel* 2006;85:1248–53.
- [18] Soria-Verdugo A, Garcia-Hernando N, Garcia-Gutierrez LM, Ruiz-Rivas U. Analysis of biomass and sewage sludge devolatilization using the distributed activation energy model. *Energy Convers Manage* 2013;65:239–44.
- [19] Yan JH, Zhu HM, Jiang XG, Chi Y, Cen KF. Analysis of volatile species kinetics during typical medical waste materials pyrolysis using a distributed activation energy model. *J Hazard Mater* 2009;162(646):651.
- [20] Li L, Zhao N, Fu X, Shao M, Qin S. Thermogravimetric and kinetic analysis of Spirulina wastes under nitrogen and air atmospheres. *Bioresour Technol* 2013;140:152–7.
- [21] Fiori L, Valbusa M, Lorenzi D, Fambri L. Modeling of the devolatilization kinetics during pyrolysis of grape residues. *Bioresour Technol* 2012;103:389–97.
- [22] Di Blasi C, Branca C, Santoro A, Gonzalez Hernandez E. Pyrolytic behavior and products of some wood varieties. *Combust Flame* 2001;124:165–77.
- [23] Cai J, Liu R. Weibull mixture model for modeling nonisothermal kinetics thermally simulated solid-state reactions: application to simulated and real kinetic conversion data. *J Phys Chem* 2007;111:10681–6.
- [24] Cai J, Ji L. Pattern search method for determination of DAEM kinetic parameters from nonisothermal TGA data of biomass. *J Math Chem* 2007;42:547–53.
- [25] Mani T, Murugan P, Mahinpey N. Determination of distributed activation energy kinetic parameters using annealing optimization method for nonisothermal pyrolysis of lignin. *Ind Eng Chem Res* 2009;48:1464–7.
- [26] Miura K. A new and simple method to estimate $f(E)$ and $k_0(E)$ in the distributed activation energy model from three sets of experimental data. *Energy Fuel* 1995;9:302–7.
- [27] Munir S, Daood SS, Nimmo W, Cunliffe AM, Gibbs BM. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. *Bioresour Technol* 2009;100:1413–8.
- [28] Tonbul Y, Saydut A, Yurdako K, Hamamci C. A kinetic investigation on the pyrolysis of Seguruk asphaltite. *J Therm Anal Calorim* 2009;95:197–202.